NASA TT F-11,586

SPECTROPHOTOMETRIC DETERMINATION OF TITANIUM IN FERRO-NIOBIUM WITH DIANTIPYRYLMETHANE

R. Kajiyama and K. Yamaguchi

N68-19785

(ACCESSION NUMBER)   (THRU)

(PAGES)   (CODE)

(NASA CR OR TMX OR AD NUMBER)   (CATEGORY)

FACILITY FORM 602

SPECTROPHOTOMETRIC DETERMINATION OF TITANIUM IN FERRO-NIOBIUM WITH DIANTIPYRYLMETHANE

R. Kajiyama and K. Yamaguchi

ABSTRACT: From 0.02 to 0.60% of titanium as an impurity in ferro-niobium was determined with diantipyrylmethane as a colorimetric reagent. With this reagent, however, niobium several hundred times as much as titanium did not interfere, provided that niobium had been previously converted to its oxalate. A sample was fused with potassium pyrosulfate, and digested into a sulfuric acid solution containing ammonium oxalate. An appropriate aliquot was taken out, and iron was reduced by adding ascorbic acid. Eight ml of hydrochloric acid (1+1) and 20 ml of the 1% reagent solution were added, and the whole volume was made up to 50 ml with water. The amount of titanium was obtained by the measurement of absorbency at 385 mµ after 45 minutes.

1. Introduction

Diantipyrylmethane, which recently has come to be employed as a colorimetric /908* agent for titanium [1-5] has few interfering elements. Analytical operations with it, such as determinations in strong acids, are easy, and its sensitivity of detection is high, so it is used for determining titanium in iron and other metals. The authors used this agent to determine the amount of titanium in steel and, as a result, discovered that it was useful in determining the amount of titanium included as an impurity in ferro-niobium. Since the analytical chemical properties of titanium and niobium are similar to each other, the determination of titanium in niobium is difficult, and it is known that even when using spectrophotometric methods, hydrogen peroxide, pyrogallol, hydroquinone, thyron, etc. interfere with each other. However, if the niobium is converted to its oxalate and diantipyrylmethane is used, the analysis is easy to perform even if several hundred times more titanium is present, and an accurate determination can be made. The authors investigated the basic conditions for ferro-niobium analysis, established an analytical procedure and obtained good results in the analysis of several types of samples, which are reported here.

2. Reagents and Equipment

2.1 Reagents

Diantipyrylmethane solution: 10g of diantipyrylmethane was dissolved in /909 300ml of sulfuric acid (1+20), diluted in 1ℓ of water and stored in a brown bottle.

Standard titanium solution (20 µg/ml): 0.167 of titanium oxide was weighed in a platinum crucible, 5g of potassium pyrosulfate was added and fused with the titanium oxide. This was then digested in sulfuric acid (1+9) to the amount of one liter and used as a stock solution. A fixed amount of this solution was dissolved in 5 times the amount of water to form a standard solution.

---

*Numbers in the margin indicate pagination in the foreign text.

Niobium solution (3mg/ml): Niobium pentoxide was fused with potassium pyrosulfate and dissolved in a (2%) ammonium oxalate solution.

Tantalum solution (1mg/ml): Tantalum pentoxide was fused with potassium pyrosulfate and dissolved in a 3% solution of ammonium oxalate containing 10ml of sulfuric acid (1+1) making one liter of solution.

Ascorbic acid solution (10w/v%): This solution was prepared when necessary.

2.2. Equipment

Photometer: Shimazu-Bousch Lomb diffraction grid type photometer, spectronic 20, cell 10.6 mm in diameter.

3. Tests

3.1. Test Procedure and Absorption Curves

3ml of standard titanium solution (60 µg titanium) was placed in a 50 ml measuring flask, 8ml of hydrochloric acid (1+1), 5 ml of ascorbic acid and 20ml of diantipyrylmethyl were added, diluted in water until 50 ml of solution was obtained, and absorbency was measured after 45 minutes. The absorption curves of the titanium-diantipyrylmethane complex obtained by this operation are shown in Figure 1. The maximum absorption occured in the vicinity of 385mµ.
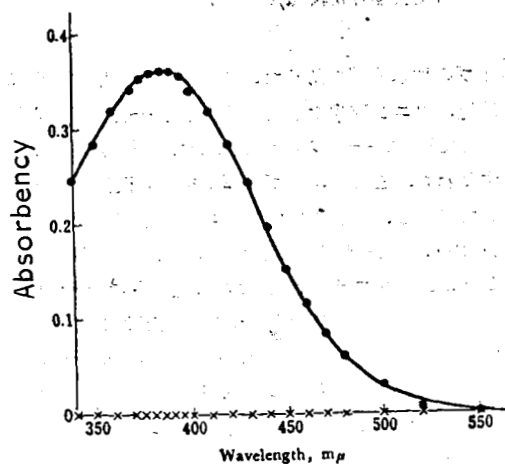

Fig. 1
Absorption Spectrum of Titanium-
Diantipyrylmethane Complex
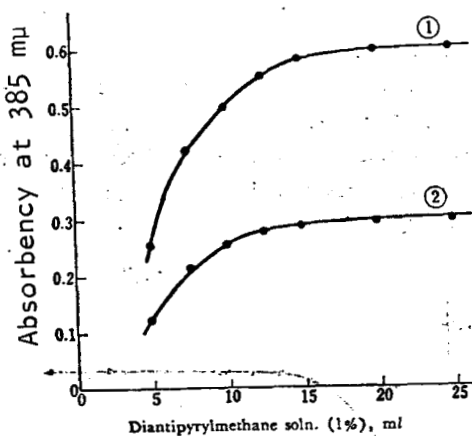
—●— Ti-diantipyrylmethane complex,
—x— Reagent blank

Fig. 2
Optimum Amount of Diantipyrylmethane
Solution (1%)

3.2. Amount of Diantipyrylmethyl Added

In accordance with the procedure in 3.1, a study was made of the amount of reagent solution added for 50 µg and 100 µg of titanium. The results are shown in Figure 2. As the amount of reagent increased, the absorption had a tendency to increase slightly, becoming fixed above 15 ml. We decided to use 20ml, keeping the amount of titanium in mind.

3.3. Effect of Acid Concentration

Generally a hydrochloric acid reagent is used, but when actually treating ferro-niobium, the use of sulfuric acid cannot be avoided, so we investigated the effects of concentrations of these acids on coloration. That is, using the procedure in 3.1, in order to study concentrations of hydrochloric acid, we measured the absorbency by varying only the acid concentration. Similarly we studied concentrations of sulfuric acid, setting the hydrochloric acid concentration at 1N, treating it by adding sulfuric acid, and measuring the absorbency. Results are shown in Figure 3. In the case of hydrochloric acid alone, when below 1.5N, when sulfuric acid is added to an HCl concentration of 1N, no variation in absorbency occurred up to the addition of 1.5N sulfuric acid.
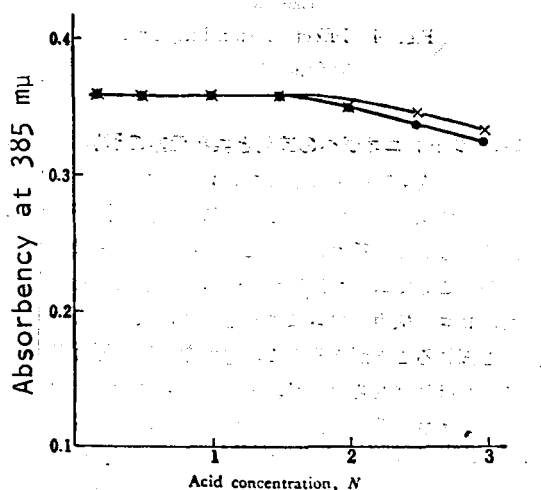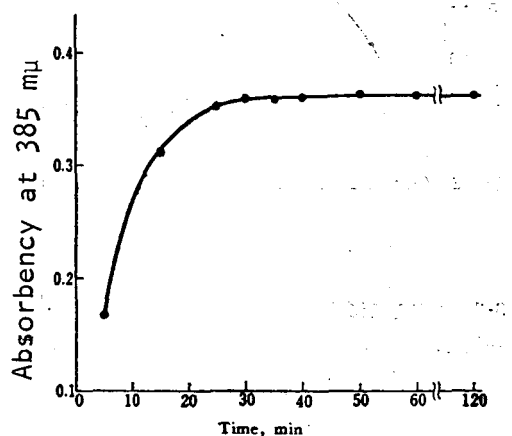

Fig. 3
Effect of Acid Concentration

Fig. 4
Effect of Standing Time

Ti 60 µg/50 ml

3.4. Stability of Coloration

A considerable amount of time is required until the coloration of the complex reached peak coloration after adding the reagent, while on the other hand, the coloration is considered to be very stable. The results of investigating the time required for maximum coloration after adding reagent in accordance with the procedure in 3.1 are shown in Figure 4. It became stable after about 30 minutes.

3.5. Applicability to Ferro-Niobium and Effects of Coexisting Elements.

We considered the application of our procedure to ferro-niobium on the basis of the above basic tests. The methods of decomposition of the sample include acid decomposition and fusion, and depending upon the various types of reagents, each has its own advantages and disadvantages. Here we decided to use the potassium pyrosulfate fusion method. In this method, the reaction is violent and frequently "boils over," so it is necessary to make sure that rapid heating does not occur. However, decomposition takes place rather easily.

Niobium precipitates very easily, so in order to make an aqueous solution, we decided to digest it in 100ml of a 2% solution of ammonium oxalate containing 5ml of sulfuric acid (1+1). By doing this, we avoid the precipitation of niobium and can treat 0.2-0.5 g of sample.

In addition to the titanium in the solution being treated in this manner, there are impurities in the niobium, tantalum, and iron, namely, aluminum, manganese and tin, so we investigated the effects caused by these elements.

3.5.1 Niobium, Tantalum.

Commercial ferroniobium contains 60% niobium, and tantalum in the amount of 10% of the amount of niobium. We placed 50ml of the niobium or tantalum solution prepared in accordance with 2.1 into a measuring flask, treated it in accordance with the procedure in 3.1, and investigated the effects. The results are shown in Figure 5 where it can be seen that there was no effect up to 36mg of niobium and 10mg tantalum. Also, there was no influence within the range of 0.1 to 0.5% for the oxalic acid concentration.

In order to prevent the hydrolysis of niobium, there are general methods being employed which use, in addition to oxalic acid, salts of tartaric, and citric acid [10,11]; we also studied the effects of these salts. That is, we fused 0.2g of niobium pentoxide with potassium pyrosulfate, and digested these respectively in 100ml of tartaric or citric acid (each 2.5%). Then we added 10ml each to a 50ml measuring flask, appropriately added tartaric or citric acid and prepared the correct amount. Then we measured the absorbency by treatment according to the procedure in 3.1. The amount of niobium in the solution being studied was 40mg, which is approximately the same amount as the niobium and tantalum obtained when treating 0.2g of ferroniobium in accordance with the analytical procedure described in 4.1 below.

The results of the tests, as shown in Table 1, show that in the case of both tartaric and citric acids, when the amount of additive is small, high
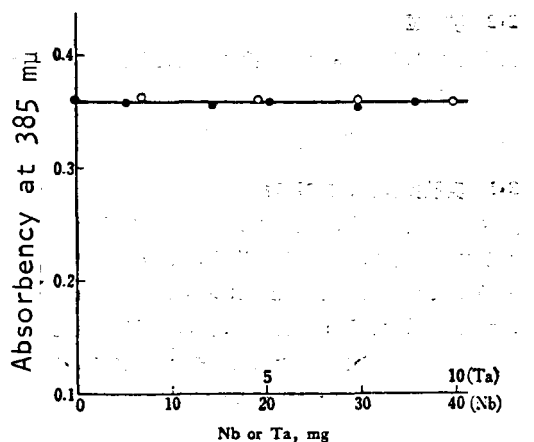
values are obtained, and as the amount of additive is increased, it is possible to reduce the influence of niobium, but in order to eliminate the effects of niobium, or the long time required for the coloration of titanium, the most effective method was to use a salt of oxalic acid.

3.5.2. Iron.

It is possible to eliminate the influence of iron by reduction to a valence of II using ascorbic acid. Using the procedure in 3.1, iron was added, and we studied the relationship between the ascorbic acid used for reduction and the amount of iron (III). The results are shown in Figure 6. By adding 5ml of 10% solution, we were able to eliminate its effect up to 50mg of iron (III).

3.5.3 Other Elements

Of the impurities which are included in ferro-niobium, the metals described above occur in the greatest amount, to a degree of several percent, so we studied them. That is, we added these elements in accordance with the procedure in 3.1 and as the results in Table II indicate, there is absolutely no influence in the amounts which normally occur.
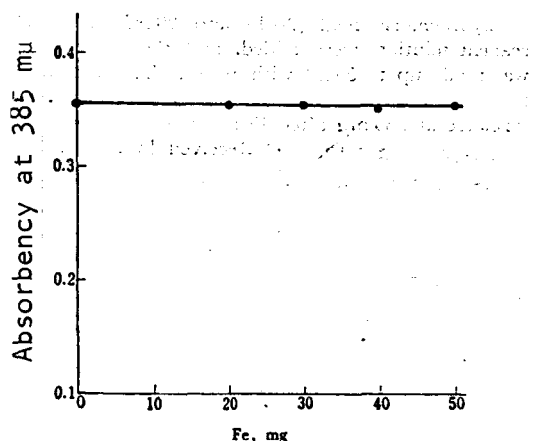

Fig. 5
Effect of Niobium and Tantalum

—●— Nb, —O— Ta, Ti 60 μg/50 ml,
Oxalic acid 0.4% w/v

Fig. 6
Effect of Iron with 5 ml of Ascorbic
Acid Solution (10%)

Ti 60 μg/50 ml

Table I

EFFECT OF MASKING REAGENT FOR NIOBIUM

Reagent	%	30 min	45 min	60 min	90 min	120 min
(Ti only)		0.355	0.356	0.356	0.356	0.357
Oxalate	0.4	0.350	0.355	0.355	0.355	0.360
Tartrate	0.5	0.750	0.750	0.750	0.750	0.750
"	1.0	0.565	0.575	0.580	0.580	0.580
"	1.5	0.490	0.500	0.510	0.510	0.510
"	2.0	0.465	0.478	0.482	0.485	0.485
"	3.0	0.395	0.415	0.425	0.430	0.430
"	5.0	0.320	0.340	0.354	0.360	0.360
Citrate	0.5	0.370	0.370	0.370	0.372	0.372
"	1.0	0.355	0.365	0.365	0.370	0.371
"	1.5	0.348	0.360	0.360	0.368	0.368
"	2.0	0.338	0.355	0.357	0.370	0.370
"	3.0	0.318	0.340	0.345	0.360	0.362
"	5.0	0.280	0.310	0.322	0.345	0.350

Ti 60 μg/50 ml

4. Analytic Procedure and Results of Analysis

4.1 Analytic Procedure

We measured 0.2 to 0.5g of sample in a magnetic crucible, added 5-10g of potassium pyrosulfate, and then we heated this for 15 minutes, at first at as low a temperature as possible and then gradually to 600°C. After cooling, we digested this in 50ml of warm water containing 2 grams of ammonium citrate and 5ml of sulfuric acid (1+1), and then diluted this to an amount of 100ml using a measuring flask. Then we added 10ml to a 50ml measuring flask (that is, from the solution obtained by filtering through dry filtering paper) and reduced the iron by adding 5ml of ascorbic acid (10%) and 8ml of hydrochloric acid (1+1), added 20ml of diantipyrylmethane (1%) and diluted this in water to a volume of 50ml. After mixing by agitation, we measured the absorbency after 45 minutes at a wavelength of 386 mµ [*] using the test solution for contrast, and determining the amount of titanium from detection lines which were prepared beforehand.

Table II
EFFECT OF DIVERSE IONS

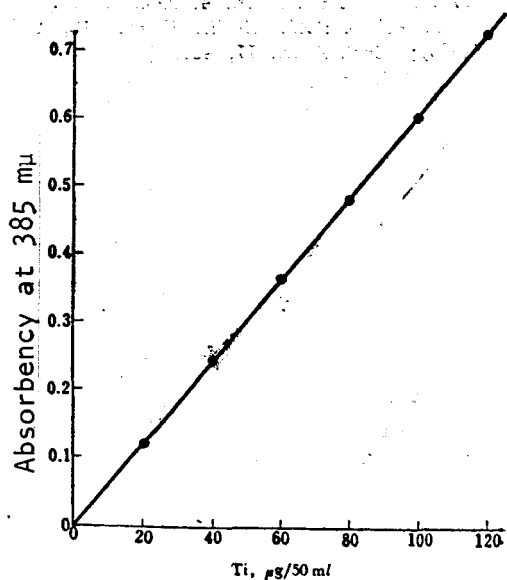| Elements	Added (mg)	$-\log T$
(Ti only)	(60 µg)	0.355
Sn	2.5	0.350
Al	5	0.357
Mn	2.5	0.355
W	1	0.355

4.2 Construction of Analytical Curve /912

Zero to 6 ml of titanium standard solution (titanium 0-120 µg) were added to a 50ml measuring flask, treated according to the procedure in 3.1 and analytical curves were constructed by finding the curves of the relationship between the amount of titanium and the absorbency. One example of this is shown in Figure 7. The molecule absorption coefficient was 1.36×10^4.

4.3 Results of Analysis

The results of analysis of several samples according to the procedure for analysis in 4.1 are shown in Table III.

Fig. 7
Analytical Curve

---

* Translators note -- apparently one line of text is missing.

6

Table III
ANALYTICAL RESULTS OF TITANIUM IN FERRO-NIOBIUM

Sample	Results (%)			Sample taken (g)
A	0.037	0.037	0.035	0.5
B	0.015	0.020	0.022	″
C	0.61	0.59	0.59	0.2
D	0.37	0.37	0.36	″
E	0.55	0.53	0.55	″

(Read at the 15th annual conference in October 1966.)

REFERENCES

1. Kakuko, Takei, Nimura Eiji, Oba Nobuo: *Gakushin* 19 Iinkai Hokoku No. 7645 (1964).
2. Polyak, L. Y.: *Zh. Analit. Khim.*, 17, 206 (1962); *J. Anal. Chem.*, *USSR.*, 17, 205 (1962).
3. Minin, A. A.: *Uch. Zap. Mololovsk Univ.*, 9, 177 (1955); *Anal. Abstr.*, 4, 2932 (1957).
4. Polyak, L. Y.: *Zh. Analit. Khim.*, 18, 956 (1963); *Anal. Abstr.*, 11 (1964).
5. Jaffery, P. G., G. R. E. C. Gregory: *Analyst*, 90, 177 (1965).
6. JIS G 1223 (1963).
7. Masao, Ryo, Mochizuki Heiichi, Kajiyama Rokuro and Misaki Tsuyoshi: *This Journal*, 4, 499 (1955).
8. Masao, Kawahata, Mochizuki Heiichi and Misaki Tsuyoshi: *op. cit.* 10, (1961)
9. Tsuneo, Shimizu and Saibara Masakuzu: *op. cit.* 13, 1000 (1964).
10. Gakushin 19 Iinkaihen: *"Handbook on the Chemical Analysis of Iron and Steel"*, vol. 7, p. 66 (1963) (Daily Industrial News Press).
11. Polyak, L. Y.: *Zh. Analit. Khim.*, 19, 1468 (1964); *Chem. Abstr.*, 62, 9787 (1965).